

Supplementary information for

Fast detection of nitroaromatics using phosphonate pyrene motifs as dual chemosensors

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1 Experimental Methods

All chemicals such as 2,4,6-trinitrophenol (TNP), 2,4-dinitrophenol (DNP), 2,4-dinitrotoluene (DNT), 4-nitrophenol (NP), 4-nitrotoluene (NT), nitrobenzene (NB), tetrakis-(triphenylphosphine)palladium(0) [Pd(PPh₃)₄] and pyrene were of analytical grade and purchased from Sigma-Aldrich. Chemicals were used directly without further purification.

Microwave synthesis was carried out in Intelli-Vent microwave reactor with constant magnetic stirring throughout the synthesis in CEM Focused Microwave Synthesis System Discover S-Class mono mode microwave apparatus operating at a frequency of 2.45 GHz with continuous irradiation power from 0 to 300 W with utilization of the standard absorbance level of 120 W maximum power. A constant flow of air (*ca.* 10 psi of pressure) was maintained to ensure a close control of the temperature inside the reactor. Initially, microwave irradiation of required watts was used and the temperature is being ramped from room temperature to the desired temperature. Once this was reached the reaction mixture was held at this temperature for the required time. The reaction mixture was continuously stirred during the reaction. The temperature was measured with an IR sensor on the outer surface of the process vial. After the irradiation period, gas jet cooling cooled the reaction vessel rapidly to ambient temperature.

¹H NMR, ¹³C NMR spectra were recorded on Bruker 300 and 500 MHz NMR spectrometers and calibrated using TMS as internal reference. Chemical shifts are quoted in ppm. Mass spectra of the final compounds were acquired using a MALDI-Micromass Q-TOF2 equipment.

UV–Vis absorption spectra were recorded on a Perkin-Elmer (Lambda 35) UV–Vis spectrometer. Absorption spectra in solution were collected from a CHCl₃/methanol solution (conc. 1×10⁻⁶ mol/L). The spectra in the solid state were recorded from thin films of the compounds spin-coated on quartz substrates.

Steady state fluorescence emission studies were carried out in a Perkin Elmer Luminescence Spectrometer (LS-55). The fluorescence quenching experiments were carried out in a quartz cell in ethanol solution.

Stern–Volmer (SV) quenching rate constants were estimated by plotting the ratio of I_0/I to the concentration of the quencher $[Q]$, where I_0 and I are the maximum fluorescence intensity of the fluorophore before and after the addition of the analytes, respectively.

Thin films were fabricated by taking 2 mg of the fluorophore in 0.1 mL of chloroform/methanol solution and spin coated on a quartz plate with a spinning rate of 2000 rpm and annealed at 50 °C for 2 h. The fabricated thin film on the quartz plate was kept directly facing to the excitation light source while the emission spectra were collected. The position of the film was kept constant during each set of measurements.¹⁻³

The solid state fluorescence quenching performance in the vapor phase was tested under saturated vapors of NACs. Time-resolved fluorescence measurements were carried out with time-correlated single-photon counting (TCSPC) with a nanosecond LED (375 nm, pulse width <200ps) used to excite the samples.

Redox properties of the pyrene derivatives were evaluated by cyclic voltammetry (CH electrochemical analyzer). Ag/AgCl was used as the reference electrode, whereas Pt was employed as both the working and counter electrodes. Dry chloroform and tetrabutylammonium hexafluorophosphate were used as the solvent and supporting electrolyte. A ferrocene/ferrocenium (Fc/Fc^+) couple was used as the standard electrochemical reference.

The energies of the HOMO and LUMO and the corresponding band gap were calculated from the oxidation and reduction potentials. The position of the HOMO and LUMO were calculated from Eq. 1 and the band gap was determined from the difference between HOMO and LUMO.

$$\text{HOMO} = -(E_{\text{ox}} + 4.5) \text{ eV}; \text{LUMO} = -(E_{\text{red}} + 4.5) \text{ eV} \quad (\text{Eq. 1})$$

Scanning Electron Microscopy (SEM) images were acquired using Hitachi S4100 field emission gun tungsten filament instrument working at 25 kV or at high-resolution. Samples were prepared by deposition on aluminum sample holders followed by carbon coating using an Emitech K950X carbon evaporator.

Elemental analyses for C and H were performed with a Truspec Micro CHNS 630-200-200 elemental analyzer.

All quantum chemical calculations were carried out in the Gaussian 03 program by using the hybrid function B3LYP with the 6-31g* basis set.⁴

2 Chemical structures of the tested nitroaromatic and other electron deficient compounds

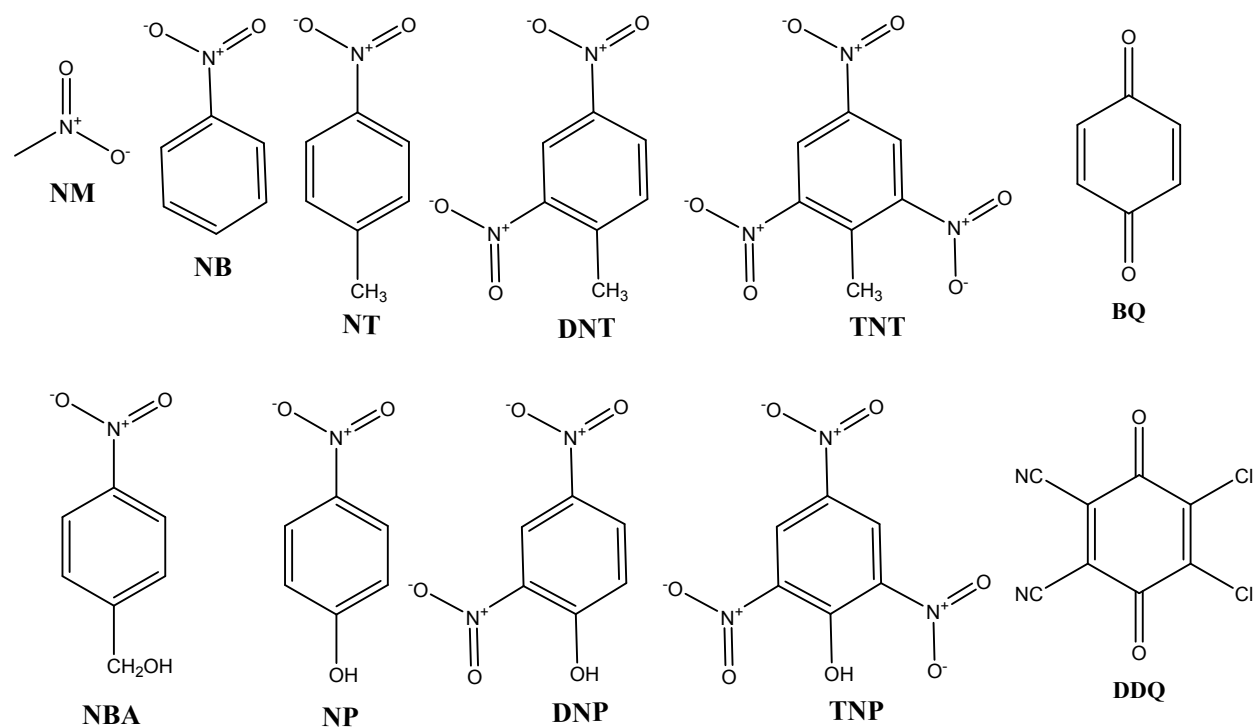


Fig. S1 Nitroaromatic and other electron-deficient compounds tested in the present work: nitromethane (NM), 4-nitrobenzene (NB), 4-nitrotoluene (NT), 2,4-dinitrotoluene (DNT), 2,4,6-trinitrotoluene (TNT), benzoquinone (BQ), 4-nitrobenzyl alcohol (NBA), 4-nitrophenol (NP), 2,4-dinitrophenol (DNP), 2,4,6-trinitrophenol (TNP), 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ).

3 Synthesis of Phosphonate pyrene derivatives and spectral characterization

3.1 Synthesis of 1,3,6,8-tetrabromopyrene ⁵

A bromine solution (0.895 g, 5.56 mmol) in nitrobenzene was added drop wise to a solution of pyrene (250 mg, 1.24 mmol) in 8 mL nitrobenzene at 120 °C under vigorous stirring. The mixture was kept at 120 °C for 4 h and then cooled to ambient temperature. The reaction mixture was then filtered and washed with ethanol three times and dried under vacuum. The light yellow colored product (516 mg, yield 81%) was insoluble in all common organic solvents.

3.2 Synthesis of octaethyl pyrene-1,3,6,8-tetrayltetrakis(phosphonate) (PE)

This synthesis was carried out using a palladium cross-coupling reaction as described in Figure 1 (see main paper). In a typical reaction setup, 1,3,6,8-tetrabromopyrene (259 mg, 0.5 mM) was transferred to a 10 mL IntelliVent microwave reactor and 2 mL of triethylphosphite and 5% tetrakis(triphenylphosphine)palladium [Pd(PPh₃)₄] was added. The reaction mixture was kept under constant magnetic stirring throughout the reaction time that occurred inside a CEM Focused Microwave Synthesis System Discover S-Class equipment. A constant flow of air (*ca.* 10 psi of pressure) ensured a close control of the temperature inside the reactor. The temperature was gradually raised to 230 °C with 100 psi for a period of 5 min. The reaction occurred over a period of 45 min at this temperature, after which time the temperature of the system was gradually decreased to the ambient one. The reaction system was composed of a clear solution and completion of the reaction was investigated through TLC with the appearance of a strong blue fluorescent spot under UV illumination. The fluorescent compound was purified in a silica column and re-crystallized from a mixture of chloroform and petroleum ether. Yield 95%. ¹H NMR (300 MHz, CDCl₃): δ 9.27 (t, 2H_{ar-1,7}, ⁵J_{HP} = 30 Hz), 9.19 (s, 4H_{ar-4,5,9,10}), 4.36 - 4.20 (m, 16H, *J* = 48 Hz, -OCH₂), 1.36-1.41 (t, 24H, *J* = 15 Hz, -CH₃). ³¹P NMR (121.49 MHz, CDCl₃): δ 17.06 (t, 4P, *J*_{P-H} = 12.1 Hz). ¹³C NMR (125.77 MHz, CDCl₃): δ 16.4 (t, *J*_{P-C} = 5 Hz, -CH₃), 62.8 (s, -CH₂), 122.9 (d, *J*_{P-C} = 5 Hz), 124.2-124.5 (m, *J*_{P-C} = 33.9 Hz), 129.19 (s), 134.9-135.0 (m, *J*_{P-C} = 18.8 Hz), 137.1 (t, *J*_{P-C} = 20.1 Hz). MALDI-TOF (MS): calculated for C₃₂H₄₆O₁₂P₄ [M+H]⁺, 747.19, found 746.1. Elemental analysis (C₃₂H₄₆O₁₂P₄): Calc (%): C, 51.48; H, 6.21; O, 25.71; P, 16.59. Found: C, 51.24; H, 6.24.

3.3 Synthesis of pyrene-1,3,6,8-tetrayltetrakis(phosphonic acid) (PO)

Octaethyl pyrene-1,3,6,8-tetrayltetrakis(phosphonate) (**PE**) (100 mg, 0.15 mmol) was taken in 50 mL of 6 M HCl solution. The reaction mixture was refluxed at 80 °C for 20 h. Once reaction completed, the mixture was diluted with methanol and remove the water and methanol under reduced pressure. The resulting yellow colour viscous oily solution was washed several times with acetone and precipitated. The precipitate was filtered and dried under high vacuum to obtain final desired pyrene-1,3,6,8-tetrayltetrakis(phosphonic acid) with 90% yield. ^1H NMR (300 MHz, D_2O): δ 8.59 (t, $2\text{H}_{\text{ar-1,7}}$, $^5J_{\text{HP}} = 6$ Hz), 8.53 (s, $4\text{H}_{\text{ar-4,5,9,10}}$) ; ^{31}P NMR (121.49 MHz, D_2O): δ 13.52 (t, 4P, $J_{\text{P-H}} = 14.5$ Hz). ^1H NMR (300 MHz, $\text{DMSO-}d_6$): δ 8.87 (broad singlet, 6H); ^{31}P NMR (121.49 MHz, $\text{DMSO-}d_6$): δ 12.97 (t, 4P, $J_{\text{P-H}} = 13.3$ Hz). ^{13}C NMR (125.77 MHz, $\text{D}_2\text{O} + \text{CD}_3\text{OD}$): δ 123.9 (t, $J_{\text{P-C}} = 41.5$ Hz), 126.04 (d, $J_{\text{P-C}} = 26.4$ Hz), 128.5 (t, $J_{\text{P-C}} = 69.1$ Hz), 133.7 (d, $J_{\text{P-C}} = 13.8$ Hz), 134.7 (t, $J_{\text{P-C}} = 33.9$ Hz). MALDI-TOF (MS): calculated for $\text{C}_{32}\text{H}_{46}\text{O}_{12}\text{P}_4$ $[\text{M}+\text{Na}]^+$, 544.94, found; 544.9. Elemental analysis ($\text{C}_{32}\text{H}_{46}\text{O}_{12}\text{P}_4$): Calc (%): C, 36.80; H, 2.70; O, 36.77; P, 23.73. Found: C, 36.73; H, 2.68.

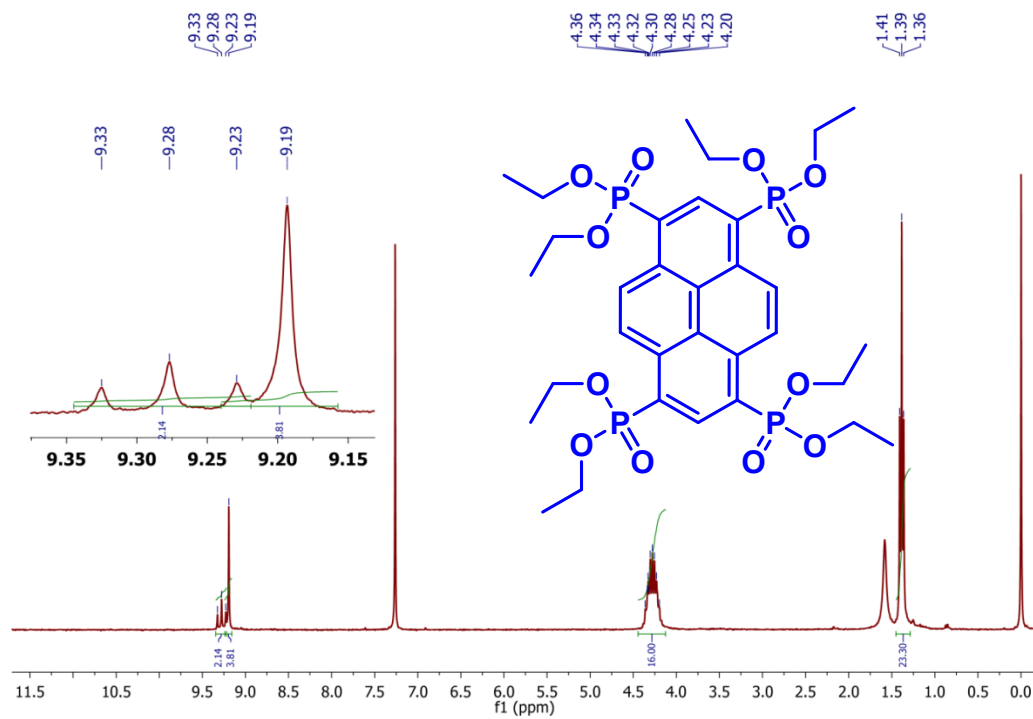


Fig. S2 ^1H NMR (300 MHz) spectrum of **PE** in CDCl_3 .

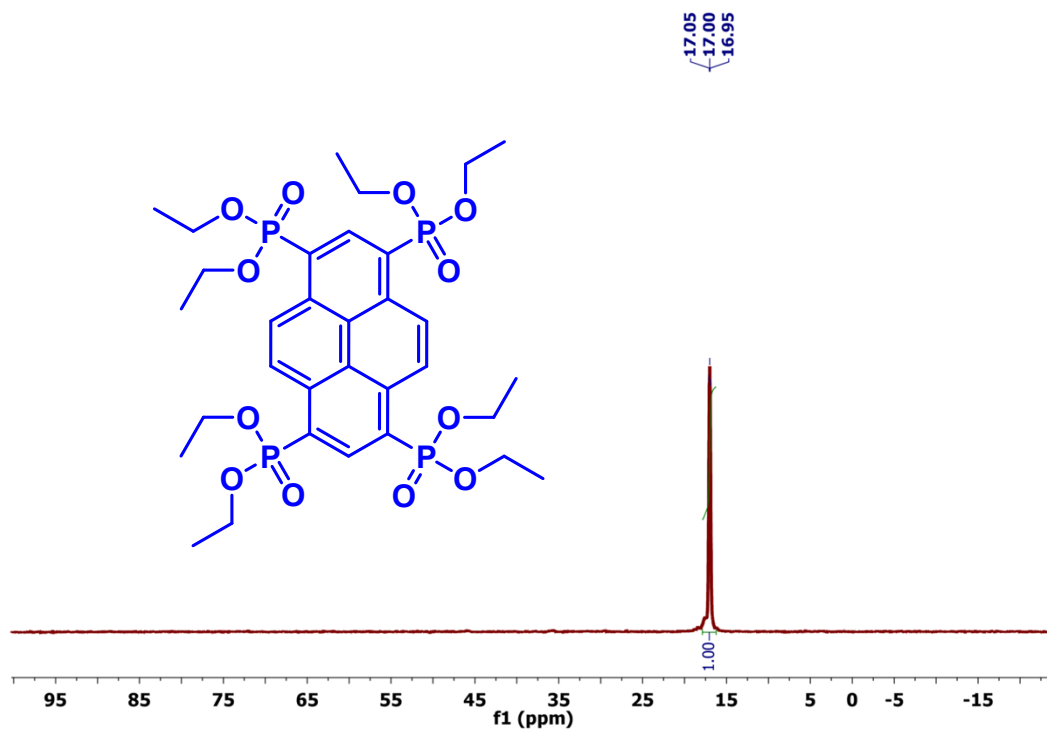


Fig. S3 ^{31}P NMR (121.49 MHz) spectrum of **PE** in CDCl_3 .

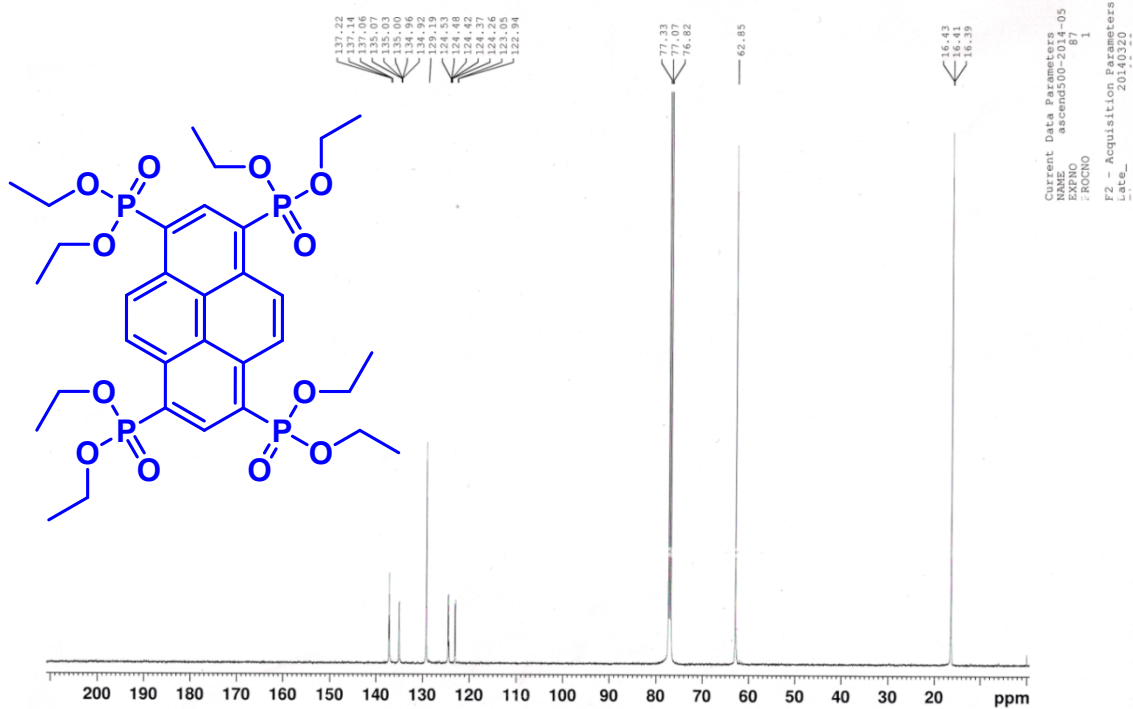


Fig. S4 ^{13}C NMR (125.77 MHz) spectrum of **PE** in CDCl_3 .

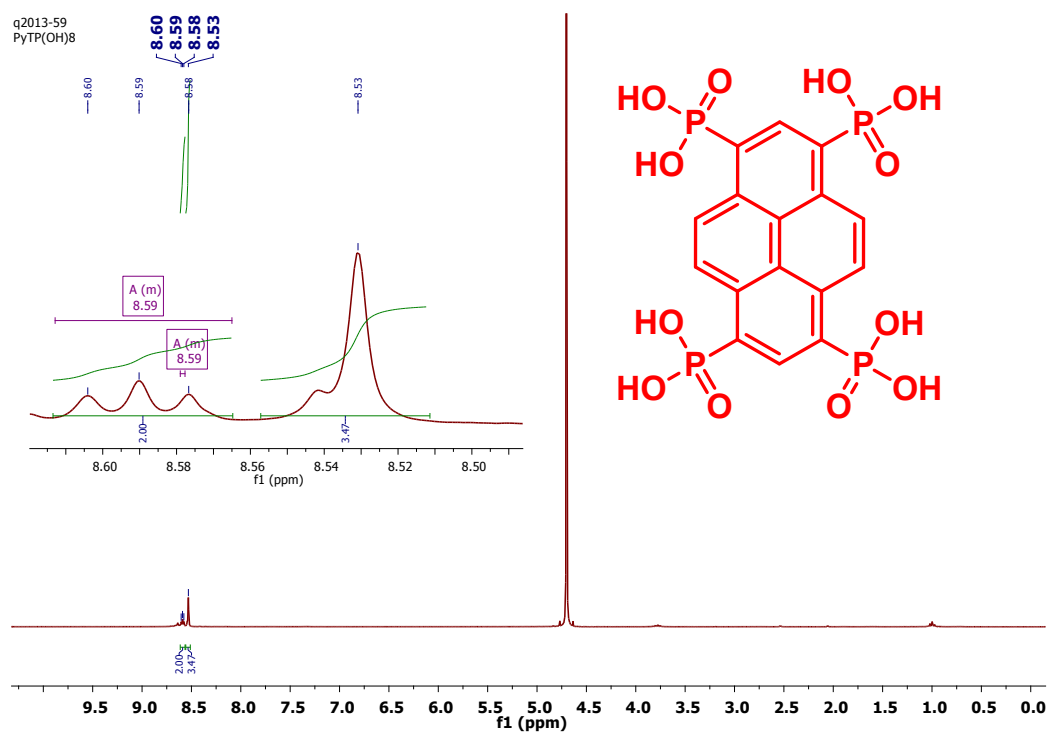


Fig. S5 ^1H NMR (300 MHz) spectrum of **PO** in D_2O .

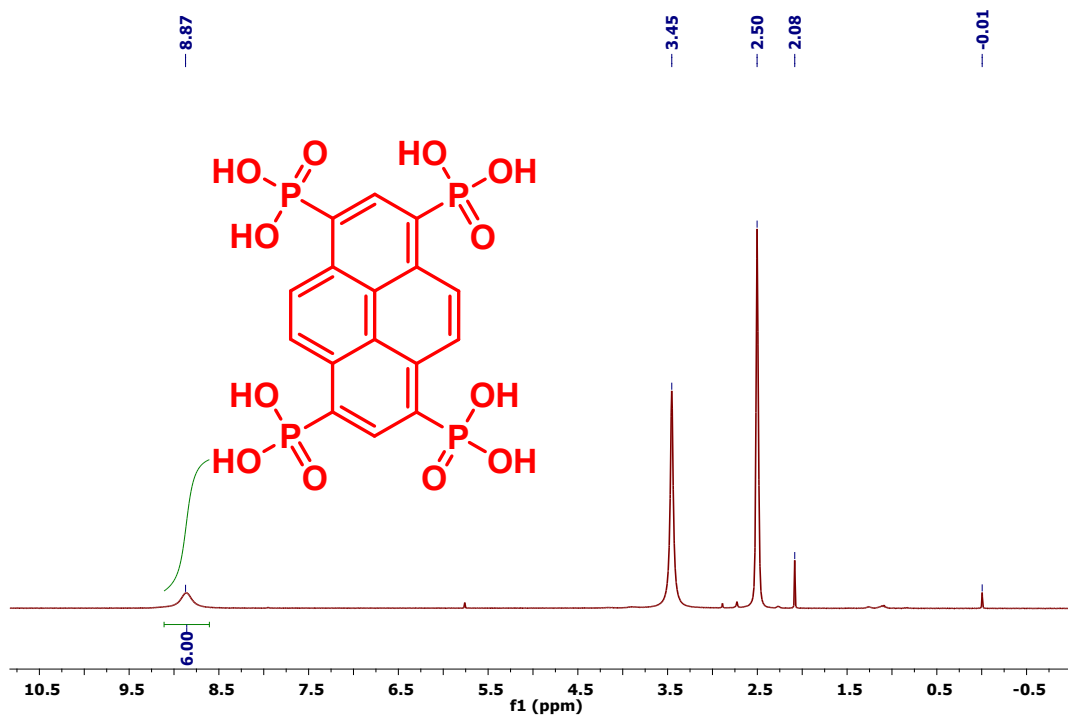


Fig. S6 ^1H NMR(300 MHz) spectrum of **PO** in $\text{DMSO-}d_6$.

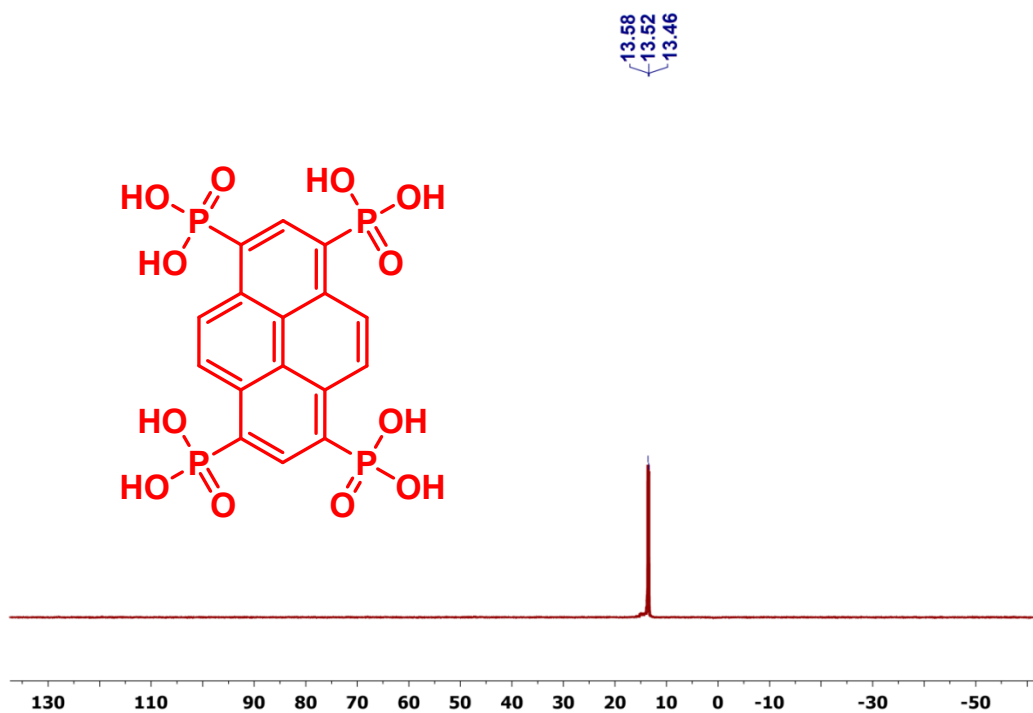


Fig. S7 ^{31}P NMR (121.49 MHz) spectrum of **PO** in D_2O .

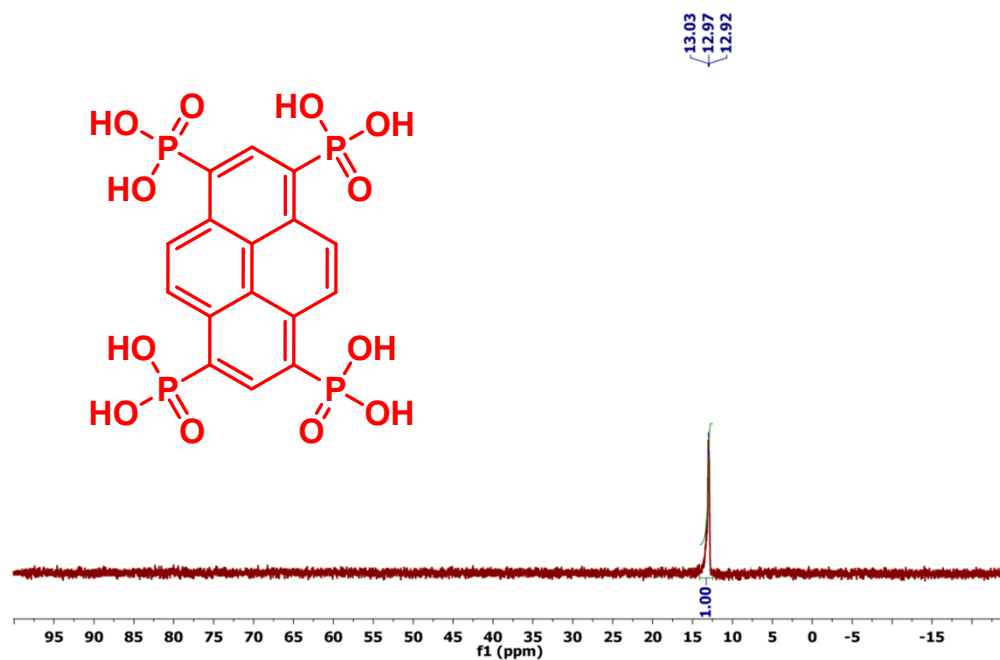


Fig. S8 ^{31}P NMR (121.49 MHz) spectrum of **PO** in $\text{DMSO-}d_6$.

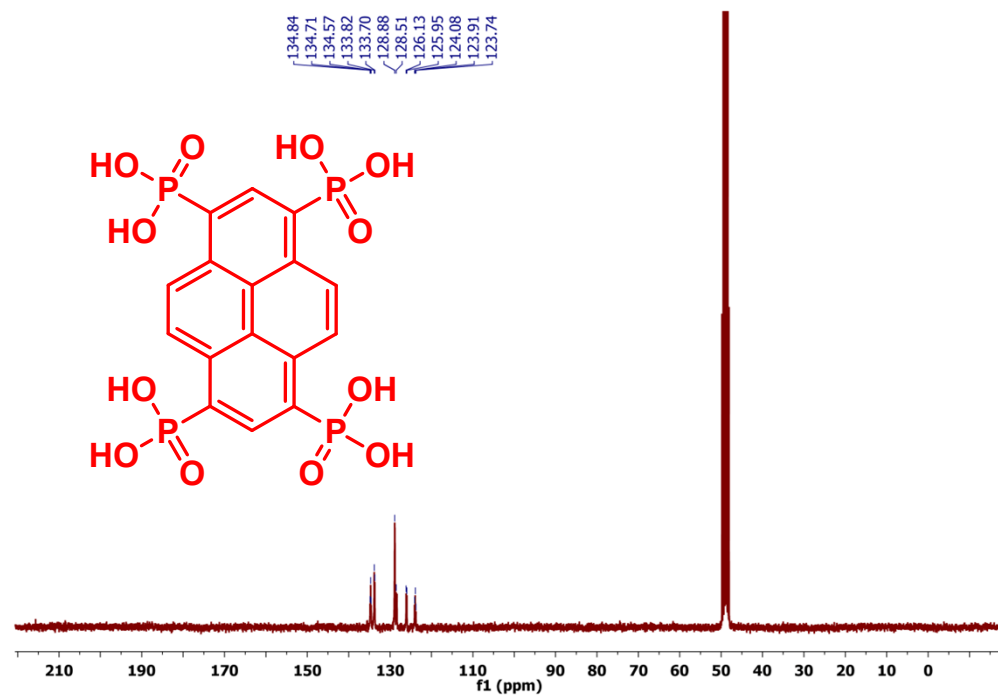


Fig. S9 ^{13}C NMR (125.77 MHz) spectrum of **PO** in $\text{D}_2\text{O}+\text{CD}_3\text{OD}$.

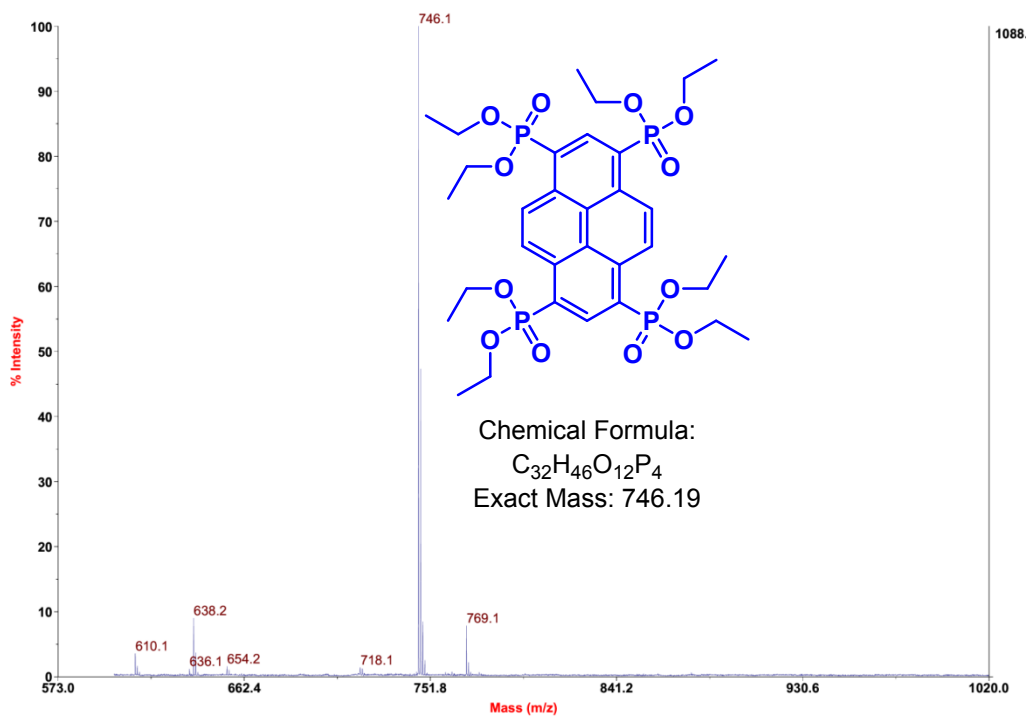


Fig. S11 MALDI-TOF mass spectrum of **PE**.

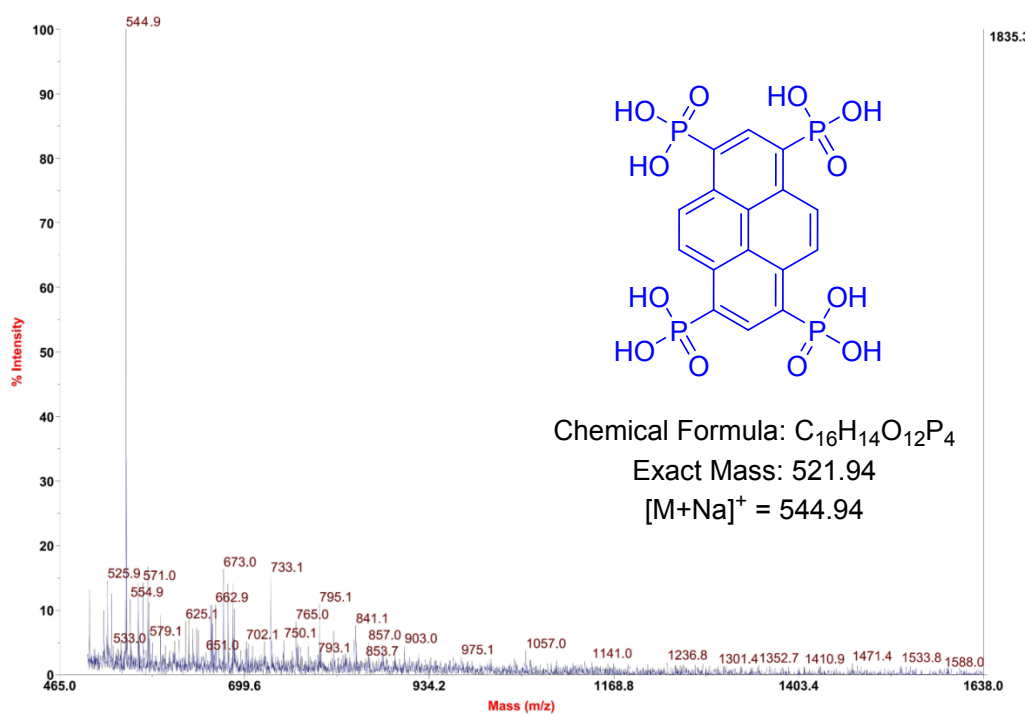


Fig. S12 MALDI-TOF mass spectrum of **PO**.

Table.S1 Summary on photophysical data of phosphonated pyrene derivatives.

Compound	Absorption (nm)		Emission (nm)		Lifetime (ns)		Stokes shift (nm)	
	solution	Thin film	solution	Thin film	solution	Thin film	solution	Thin film
PE	271, 284,	358,	386, 406,	505	3.74	0.5 (12 %)	11	132
	355, 375	376	432		(100 %)	3.6 (36 %)		
						19.5 (52 %)		
PO	272, 285,	359,	386, 406,	515	3.42	1.07 (90%)	13	140
	355, 375	378	432		(100 %)	10.1 (10%)		

4 Solvent effect on the absorption and emission properties

Fig. S13 shows the absorption spectra of **PE** and **PO** in different solvents. For both compounds, the absorption spectral features were found to be similar. On the other hand, the emission spectra of **PE** in different solvents exhibit as monomer emission with variation in the emission intensities (Fig. S14a). **PE** shows high fluorescence emission in polar solvents like THF and Ethyl acetate. Interestingly, the emission spectra of **PE** in DMF and DMSO show an overlap of the vibronic bands with decrease in the emission intensity at *ca.* 392 nm with appearance of very small and broad excimer emission at *ca.* 548 nm. This effect was more pronounced for **PO** on excitation at 330 nm in different solvents. **PO** shows strong monomer emission in water and in other polar solvents. Fig. S14c shows the emission spectra of **PO** in different alcohol solvents. As we increase the alkyl chain of the alcohol (from methanol to decanol), the monomer emission at *ca.* 392 nm decreases with appearance of new emission peak at 513 nm as an excimer emission. The excimer emission was found to be higher for decanol in comparison with other alcohols. As we increase the alkyl chain of alcohol solvent, the viscosity of solvent medium increases which restricts free orientation of the molecules. This leads to formation of excimer by close contact between the molecules. Fig. 2d shows the emission behaviour of **PO** in DMF and in DMSO, indicates a **PO** excimer emission maximum was higher than **PE**.

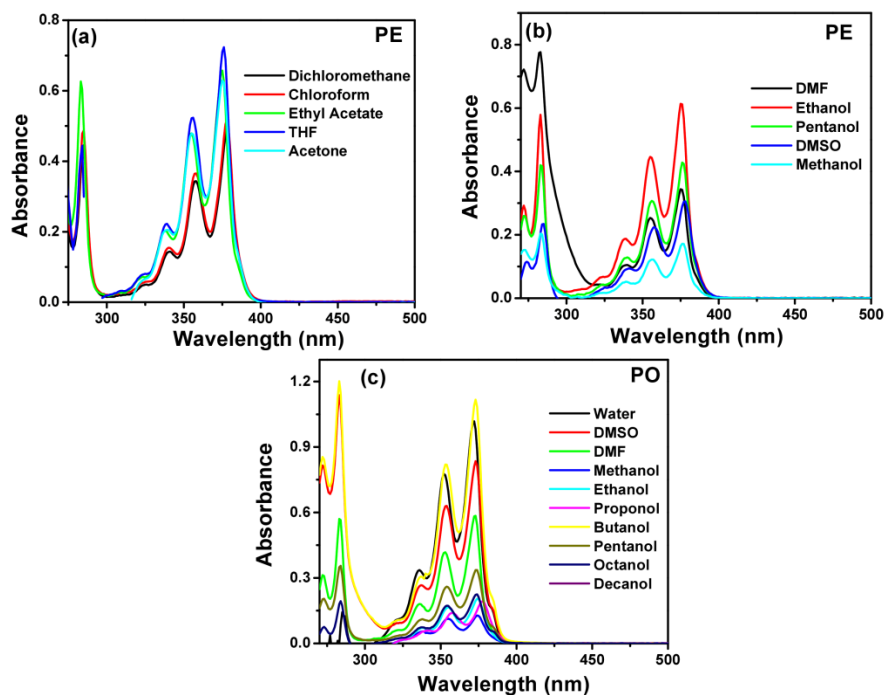


Fig. S13 Absorption spectra of PE (a and b) and PO (c) in different solvents.

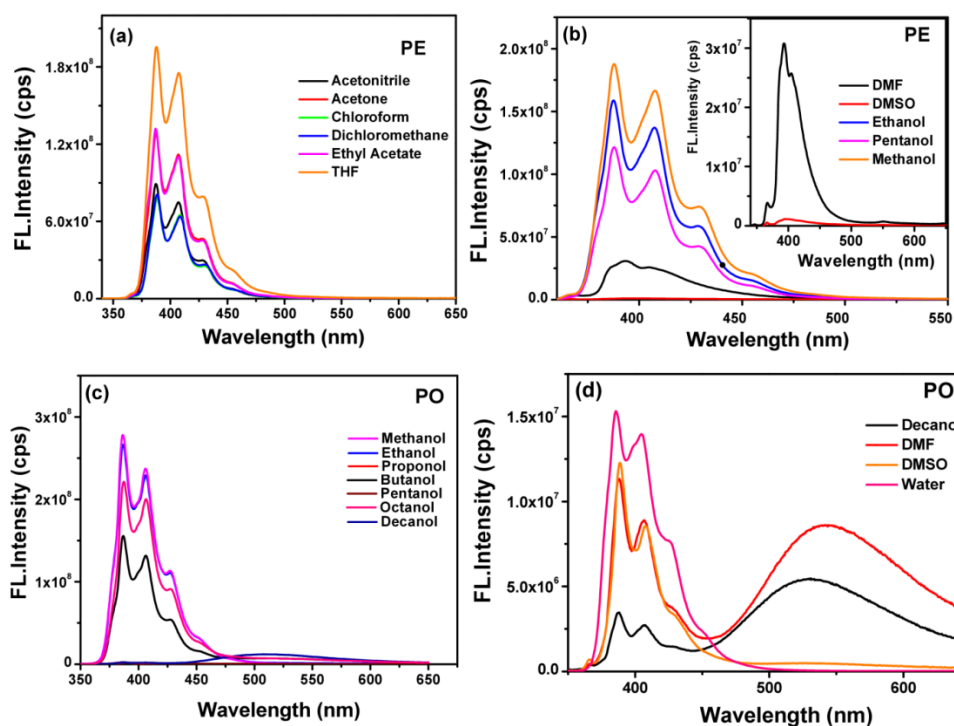


Fig. S14 Fluorescence emission spectra of PE (a and b) and PO (c and d) in different solvents on excitation at 330 nm.

5 Steady state fluorescence emission studies of pyrene derivatives treated with NACs

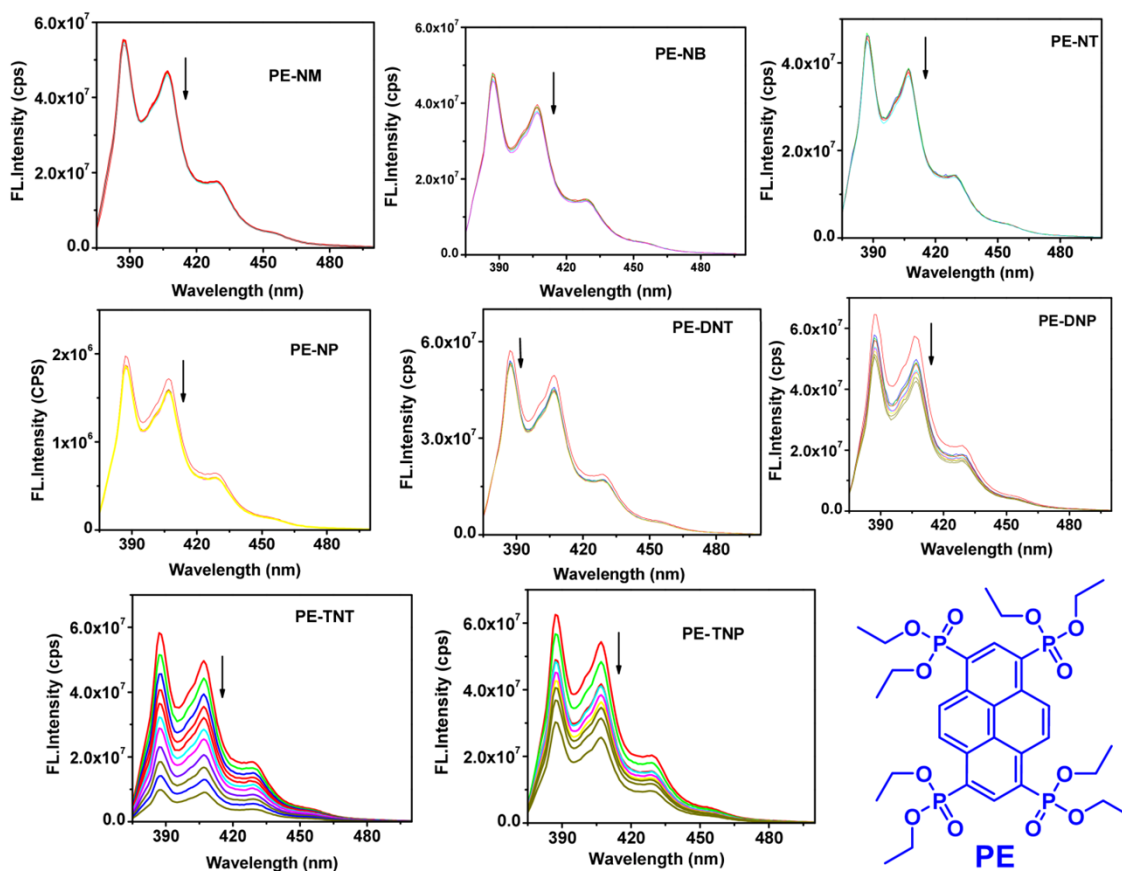


Fig. S15 Spectrofluorometric addition of **PE** (1×10^{-6} , M) with addition of different nitroaromatics (0-30 μ M) in methanol.

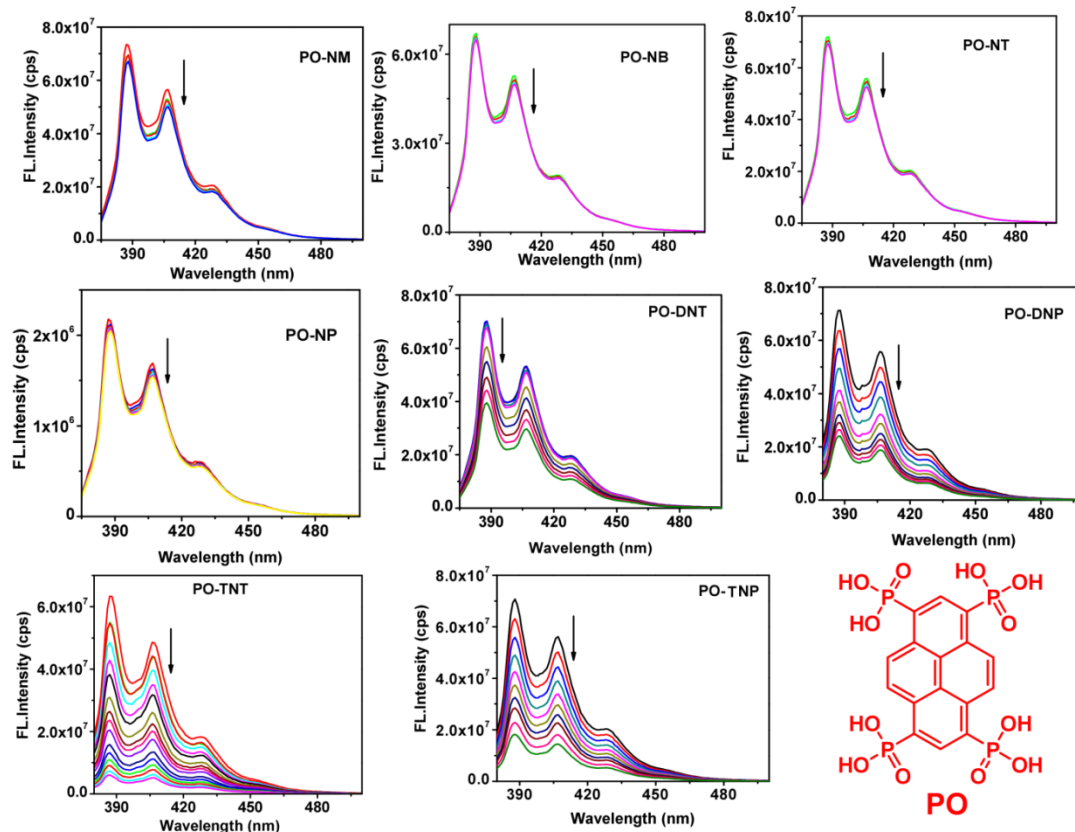


Fig. S16 Spectrofluorometric addition of **PO** (1×10^{-6} , M) with addition of different nitroaromatics (1–30 μ M) in methanol.

5 Selectivity

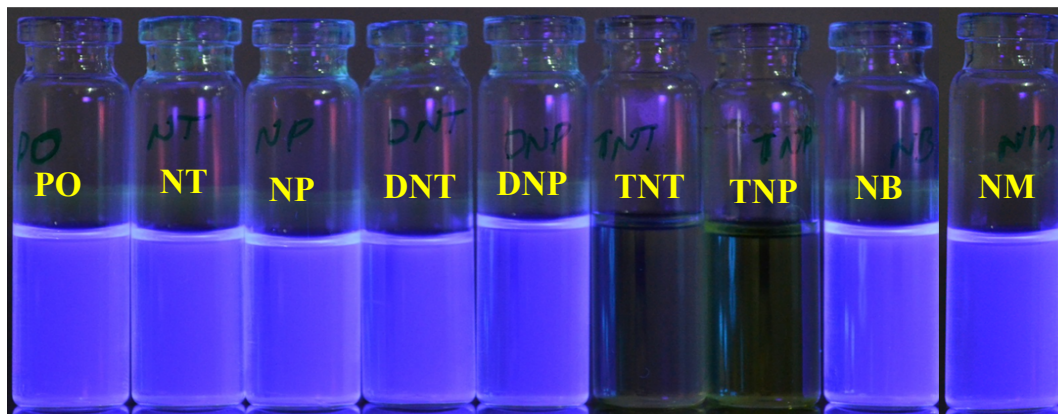


Fig. S17 Change in the fluorescent intensity of **PO** (5×10^{-6} M) upon addition of 30 μ L of various analytes under UV light at 365 nm. Legend: NT (4-nitrotoluene), NP (4-nitrophenol), DNT (2,4-dinitrotoluene), DNP (2,4-dinitrophenol), TNT (2,4,6-dinitrotoluene), TNP (2,4,6-trinitrophenol), NB (4-nitrobenzene) and NM (nitromethane).

6 Quenching efficiency

The quenching efficiency was obtained by plotting $(I_0 - I/I_0) \times 100$ to the concentration of different NACs. Where I_0 and I are the area under the curve of fluorescence emission intensities of the fluorophore before and after addition of analytes.

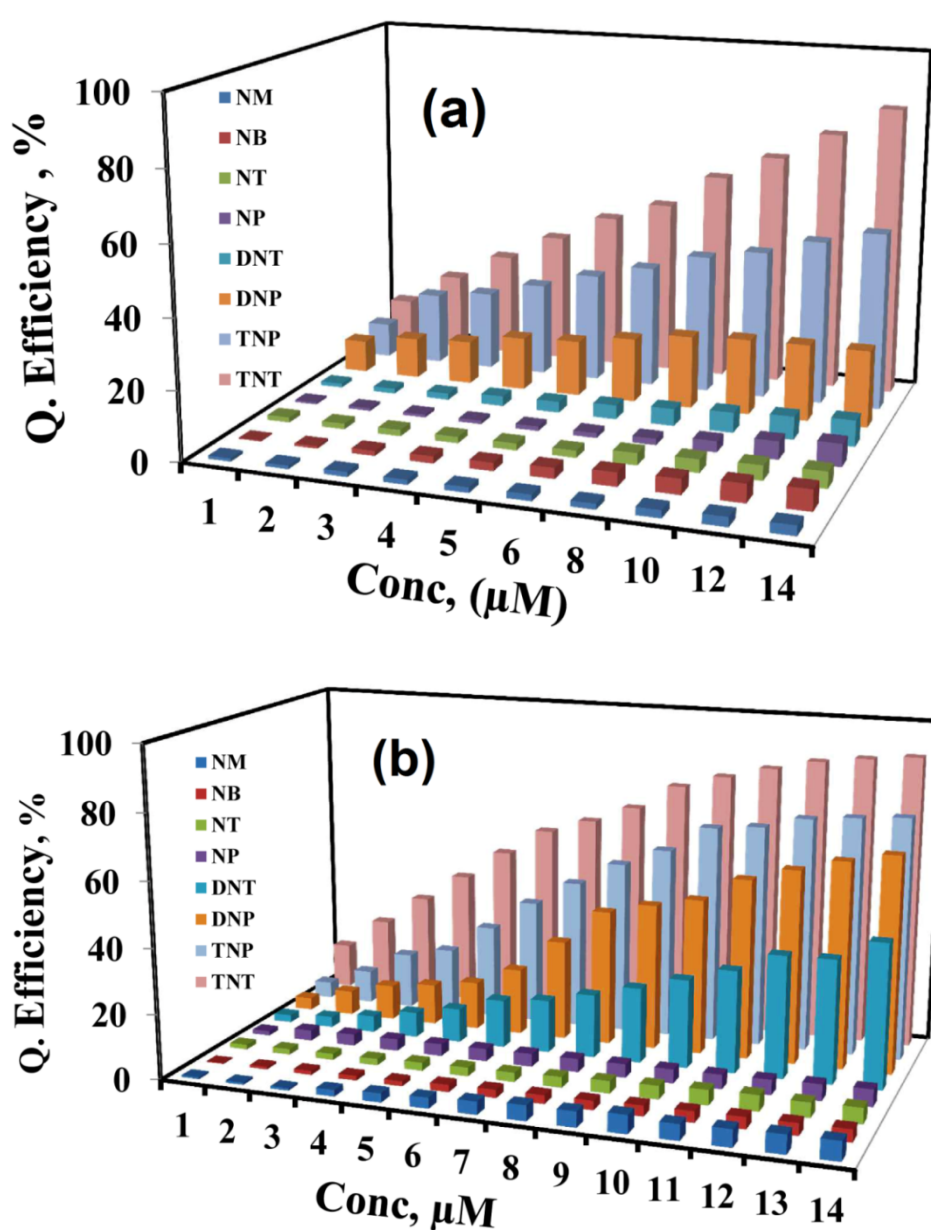


Fig. S18 Quenching efficiency of (a) **PE** and (b) **PO** at different concentrations of various NACs.

7 Determination of Stern-Volmer rate constants

The quenching behavior was studied using the Stern-Volmer equation $I_0/I = 1 + K_{sv}[Q]$, where I_0 , I are the fluorescence intensity before and after addition of the quencher, respectively, K_{sv} is the Stern-Volmer (SV) quenching rate constant and $[Q]$ is the concentration of the quencher. A linear SV response was observed for common analytes and different nitroaromatics treated with PE, ultimately indicating a static quenching phenomenon.

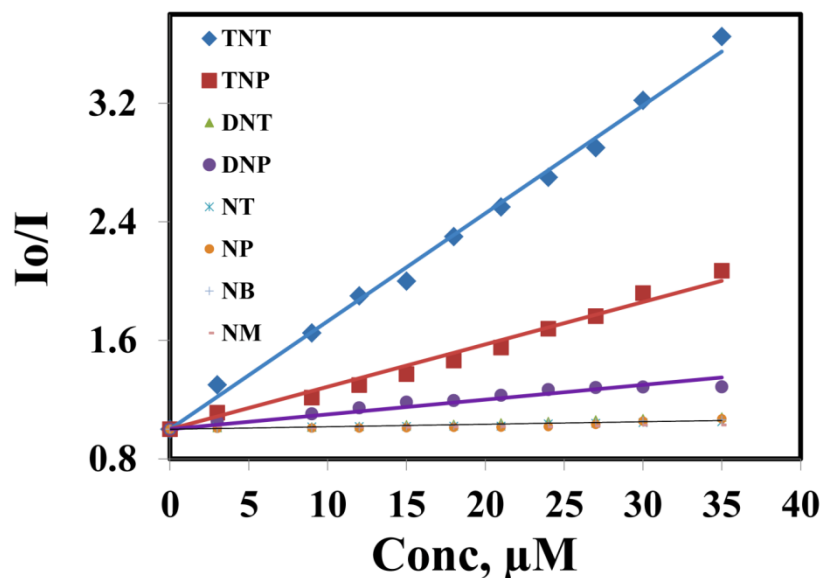


Fig. S19 Stern-Volmer (SV) plot of **PE** with different NACs at different concentration levels.

Table. S2 Summary on rate constants of **PE** and **PO** for different nitroaromatics.

NACs	PE (1×10^4 , M^{-1})	PO (1×10^4 , M^{-1})
NM	0.07	0.12
NB	0.10	0.16
NP	0.14	0.17
NT	0.17	0.22
DNP	0.22	0.89
DNT	1.02	2.06
TNP	2.86	3.62
TNT	6.69	8.35

8 UV-Visible titration study

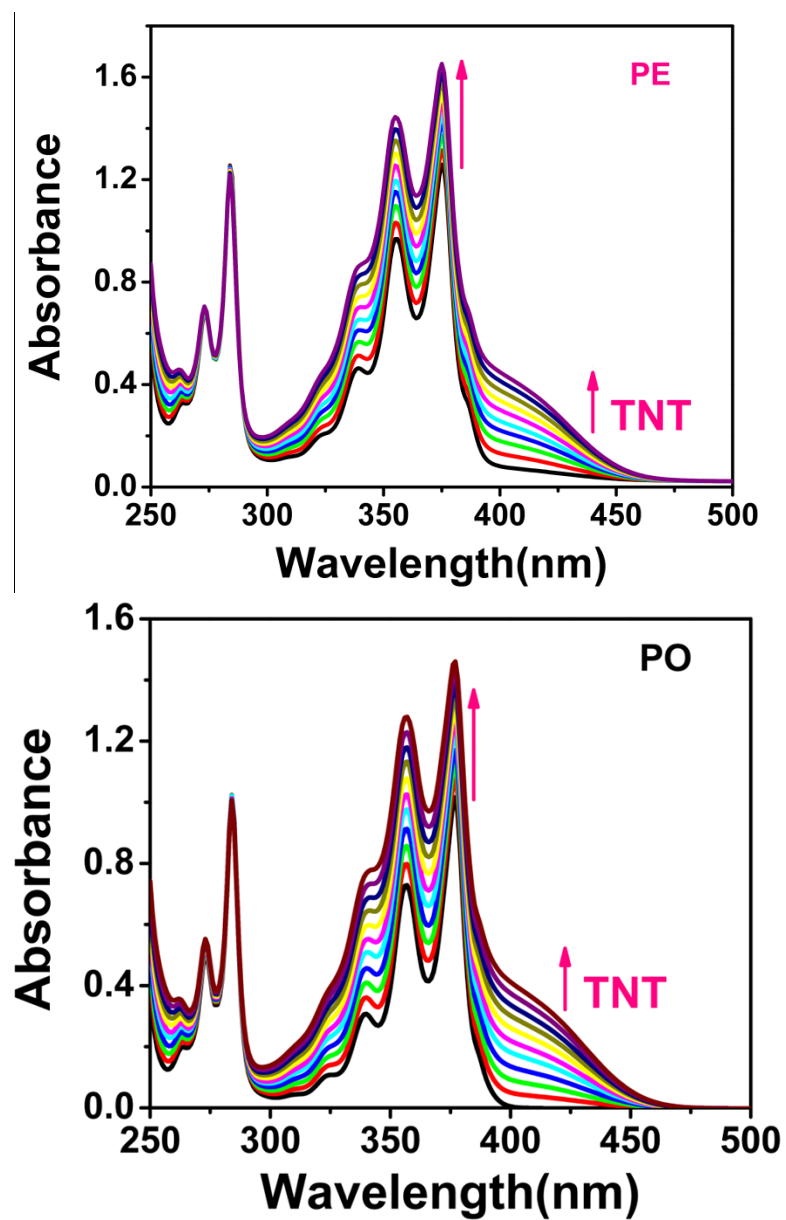


Fig. S20 Spectrophotometric titration of **PE** and **PO** upon addition of different concentrations of TNT.

9 Time-resolved fluorescence emission (TCSPC)

Time-resolved fluorescence measurements were carried out using a time-correlated single-photon counting (TCSPC) with a nanosecond LED (375 nm, pulse width < 200 ps) and a repetition rate of 1 MHz. Collected photons at the detector are correlated by time-to-amplitude converter (TAC) to the excitation pulse. Signals were collected using an IBH data station Hub photon counting module. Data analysis was performed using the commercially available DAS6 software (HORIBA JobinYvon IBH).

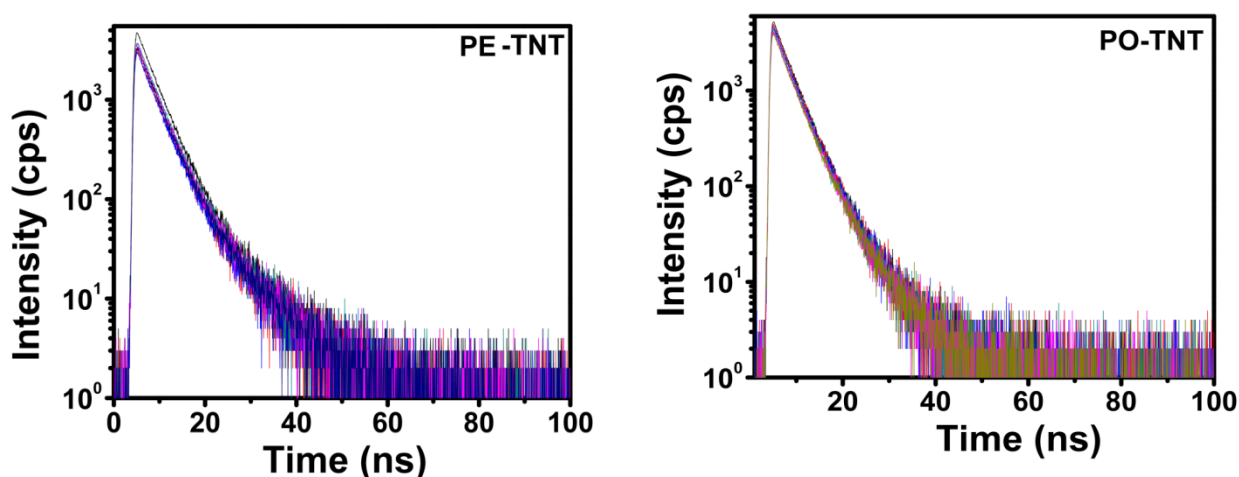


Fig. S21 Time-resolved fluorescence emission of **PE** and **PO** adducts with TNT (**PE-TNT** and **PO-TNT**, respectively) at different mole ratios of the analyte.

Table. S3 Fluorescence lifetime data of pure **PE** and **PO** at different mole ratios of TNT

mole ratio Vs PA	PE (ns)	PO (ns)
	τ_1	τ_1
0	3.74	3.46
1:0.25	3.76	3.25
1:0.5	3.77	3.08
1:0.75	3.78	2.89
1:1	3.81	2.73
1:2	3.81	2.52
1:4	3.81	2.34

10 Density functional theory (DFT)

The molecular structure of pyrene (**Py**), **PE** and **PO** were geometrically optimized using Gaussian 03 with 6-31g* as basis set.⁴ Electron density distribution of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are generated from the optimized structure with Gauss View 5.0.8. The energy level diagram was generated from the HOMO and LUMO of **Py**, **PE** and **PO** with redox potentials of different NACs.

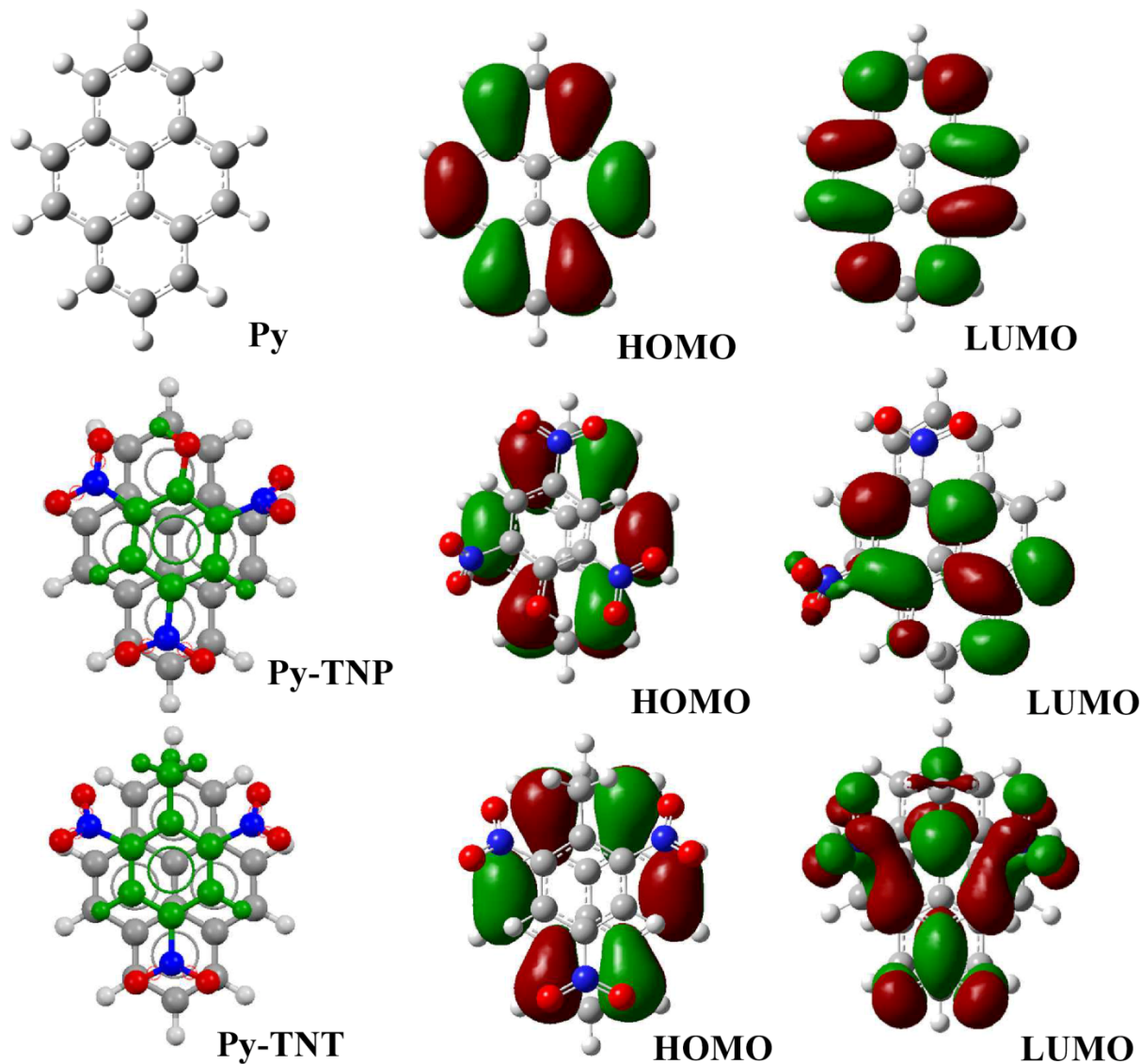


Fig. S22 The optimized structures of pyrene (**Py**) and its adducts with TNT and TNP at B3LYP/6-31g* basis set.

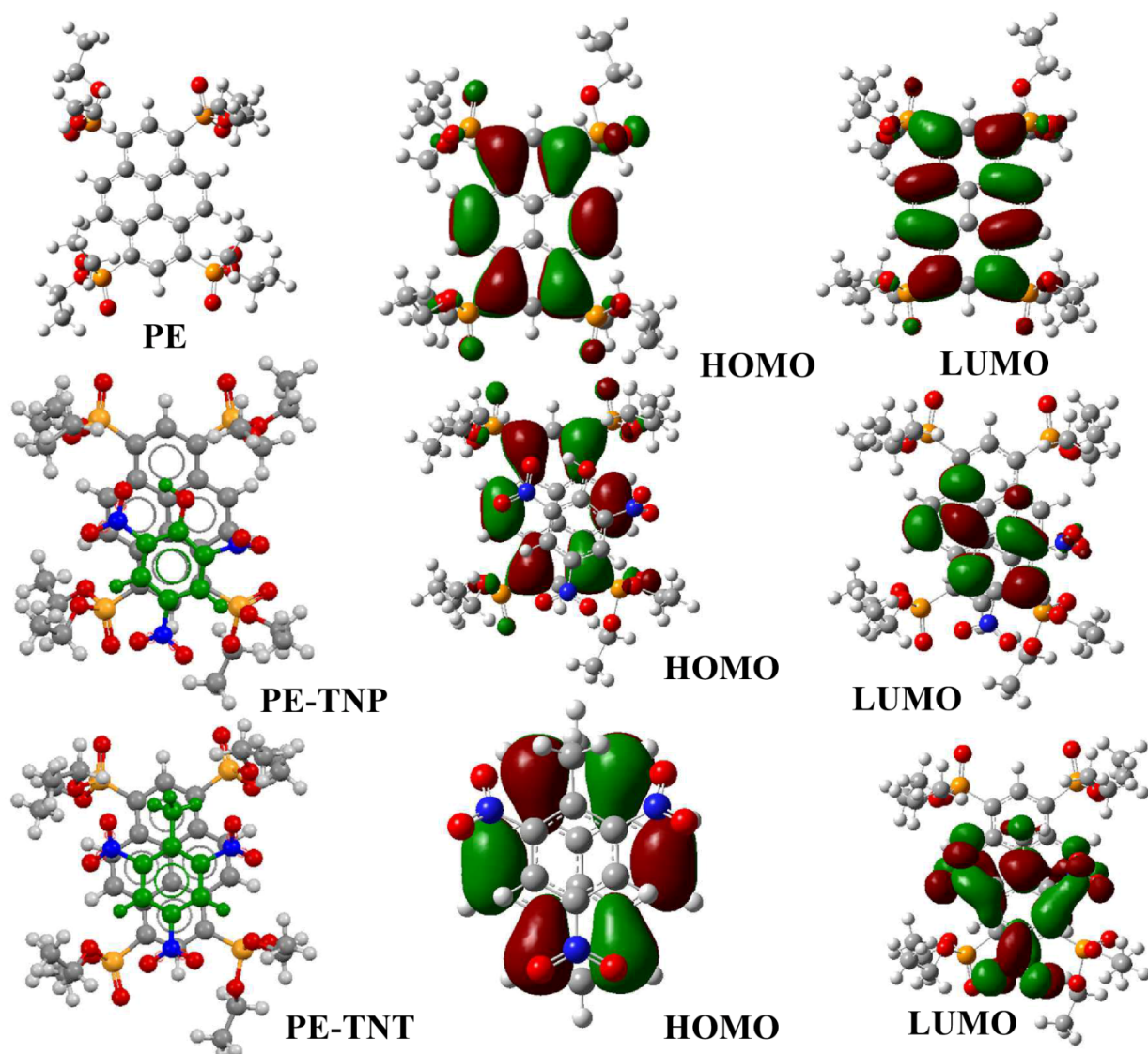


Fig. S23 Optimized structures of **PE** and it's adducts with TNT and TNP at B3LYP/6-31g* basis set.

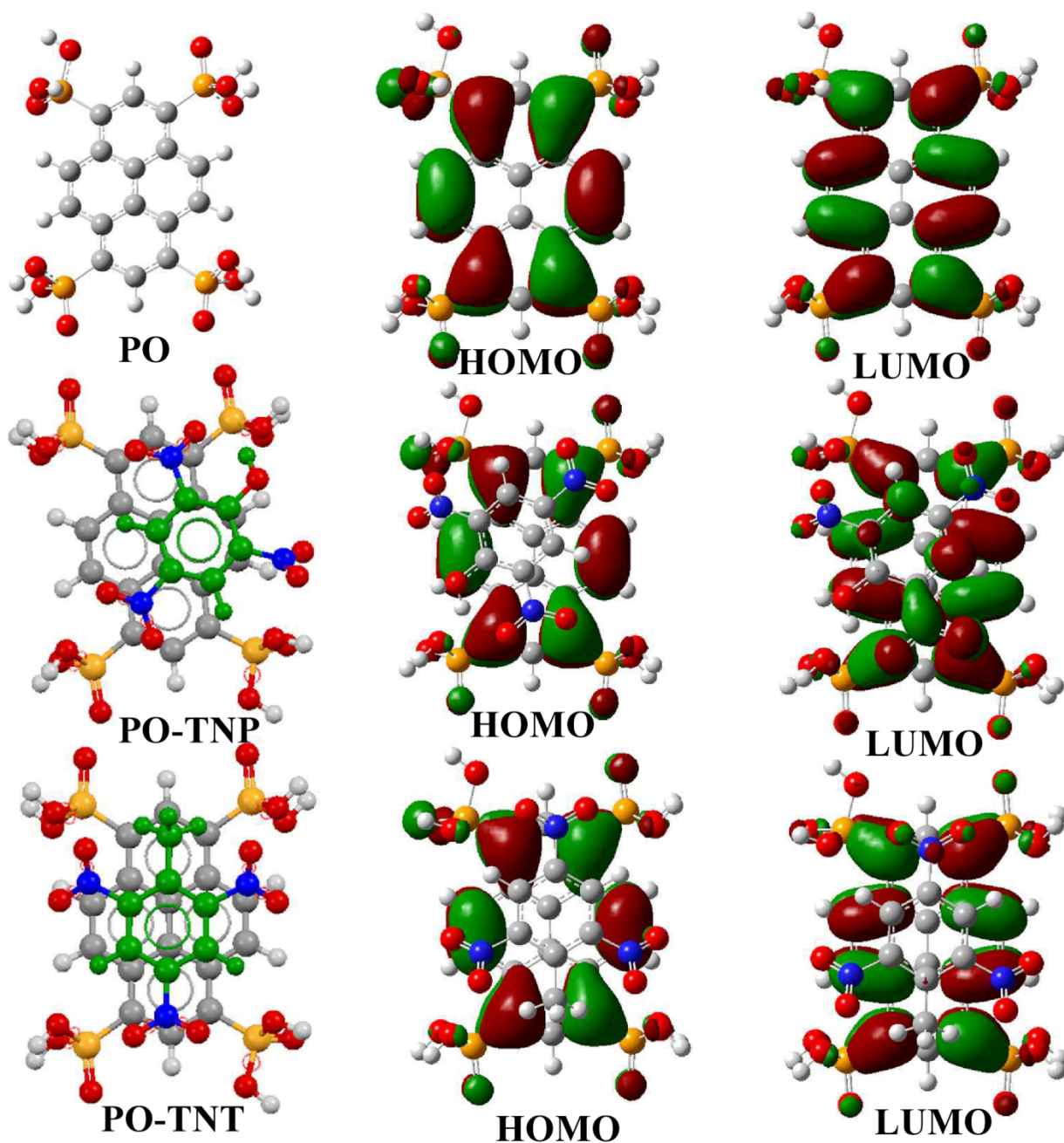


Fig. S24 Optimized structures of **PO** and it's adducts with TNT and TNP at B3LYP/6-31g* basis set.

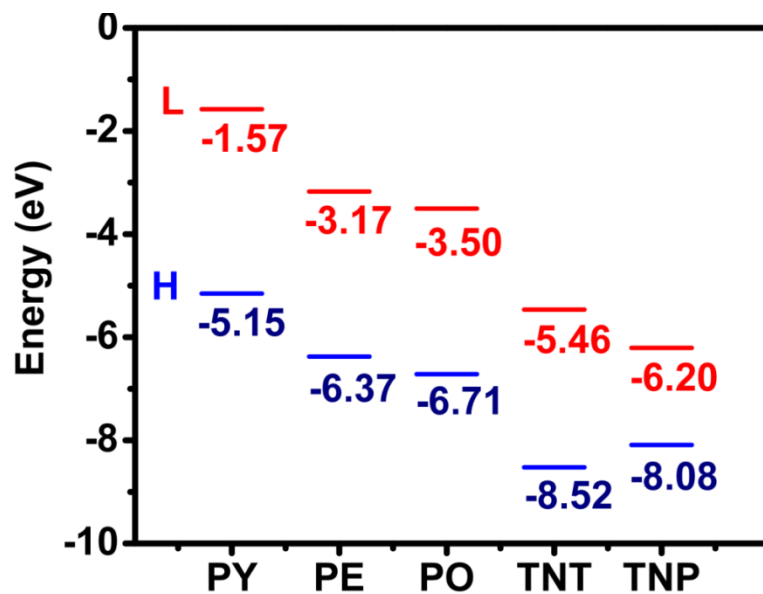


Fig. S25 Energy level diagram of Pyrene (**Py**) and its derivatives (**PE** and **PO**) and NACs (**TNT** and **TNP**).

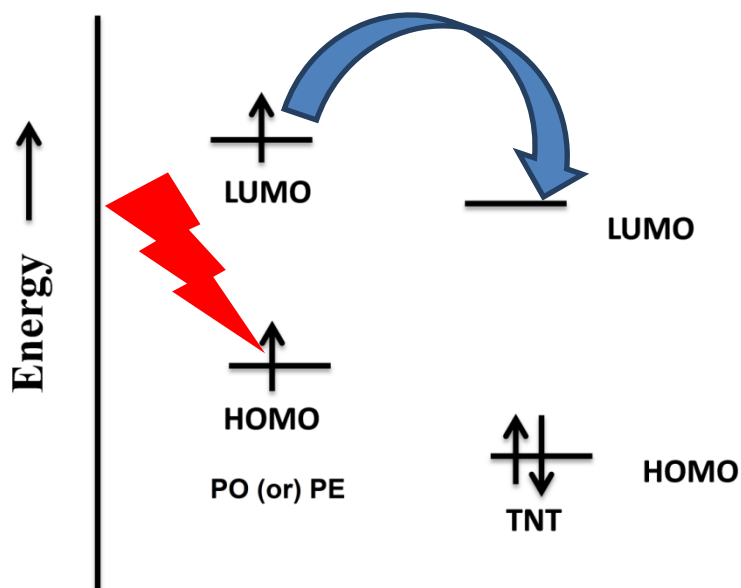


Fig. S26 Proposed mechanism of the photo-induced electron transfer (PET) from **PO** or **PE** to the quencher (**TNT**).

11 Electrochemical properties

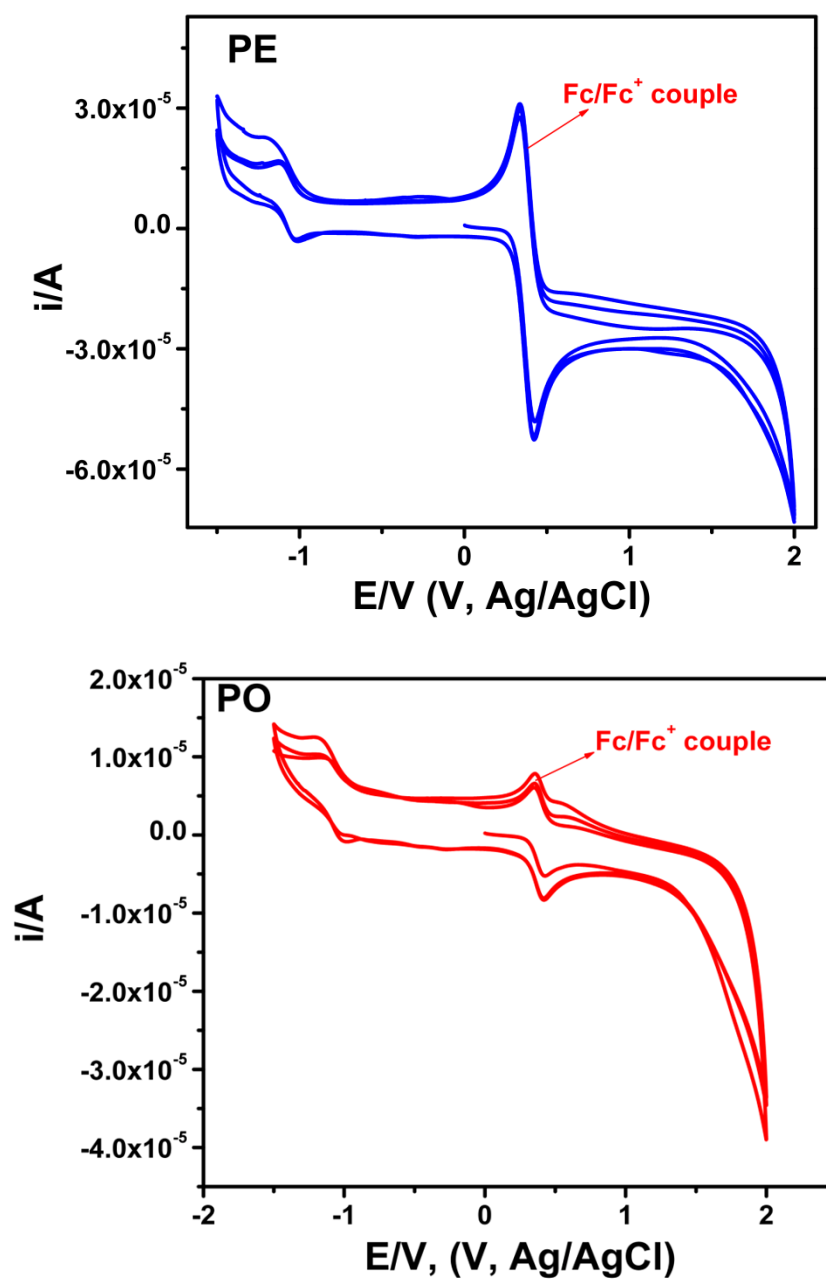


Fig. S27 Cyclic voltammogram of **PE** and **PO**, with reference to Fc/Fc⁺ couple, in the presence of Ag/AgCl electrode.

12 NMR titration study

NMR titration studies were carried out to understand the mode of interaction between phosphonated derivatives of pyrene and TNT. Studies were conducted by keeping **PE** and **PO** at fixed concentrations while varying the concentration of TNT. The variation in the aromatic proton signals and of the –OH group (for the case of the **PO** molecule) was monitored. For **PO**, the study was carried out in both D₂O and DMSO. When using D₂O, changes in the aromatic proton signals (4,5,9,10 positions) were markedly visible. The signal from the –OH group was, however, overlapped with the solvent peak. In this fashion the study was also carried out DMSO-*d*₆ to probe intermolecular hydrogen bonding between the –OH groups of **PO** (donors) and the –NO₂ groups (acceptors) of TNT. Upon addition of TNT to **PO**, the intensity of the –OH peak was broadened gradually as a function of the TNT concentration, and an apparent shift in the position of the broad signal indicates formation of π - π stacking interactions and intermolecular hydrogen bonding between donor and acceptor.

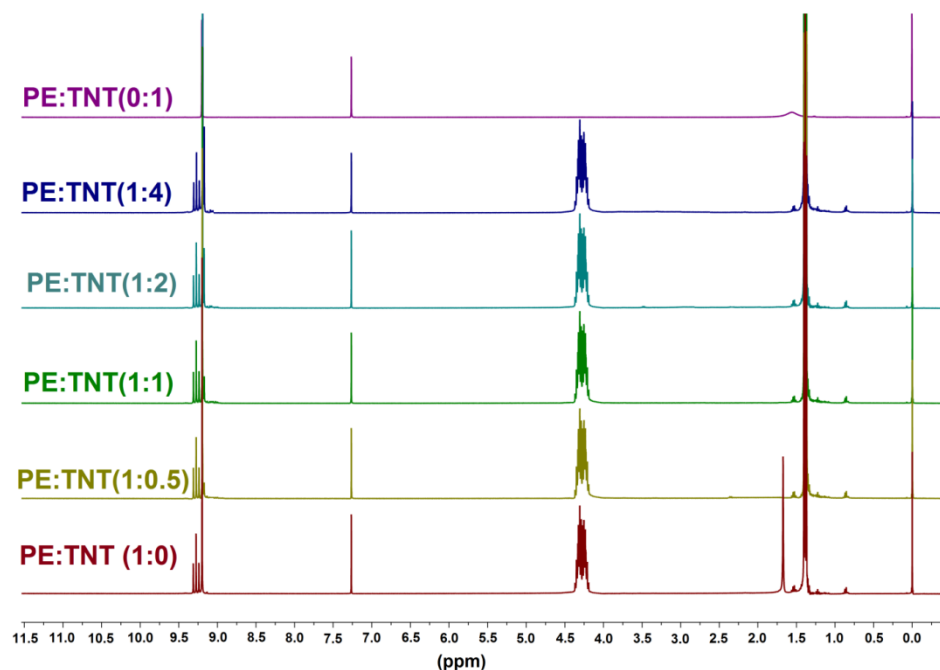


Fig. S28 ^1H NMR (300 MHz) spectra of **PE** upon addition of different mole ratios of TNT in CDCl_3 .

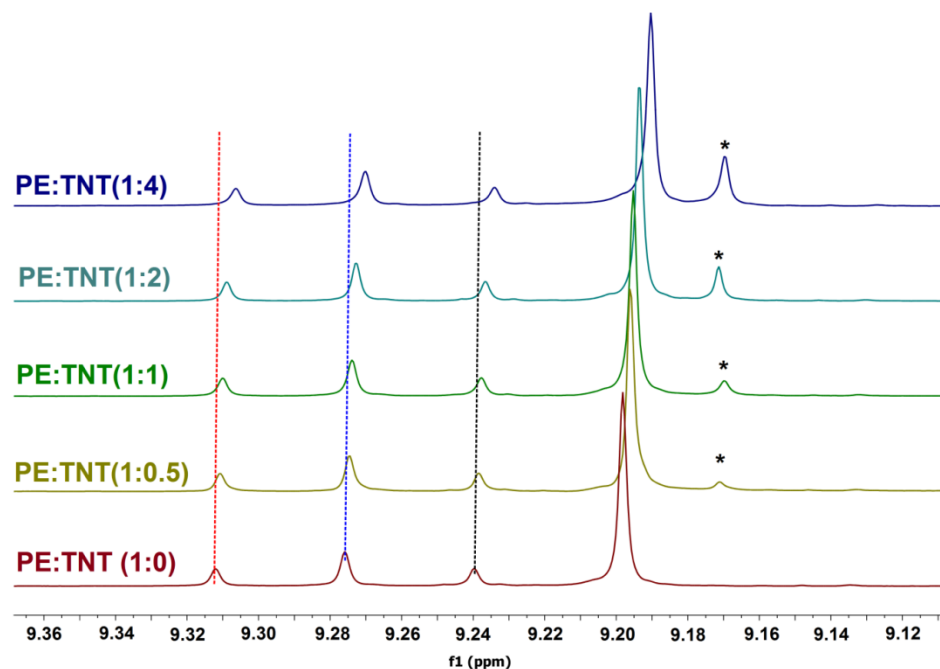


Fig. S29 Magnification of the ^1H NMR spectra of **PE** in the aromatic region showing the effect of the addition of different mole ratios of TNT to **PE** (in CDCl_3). The asterisk (*) represents the singlet peak belonging to TNT present in the aromatic region.

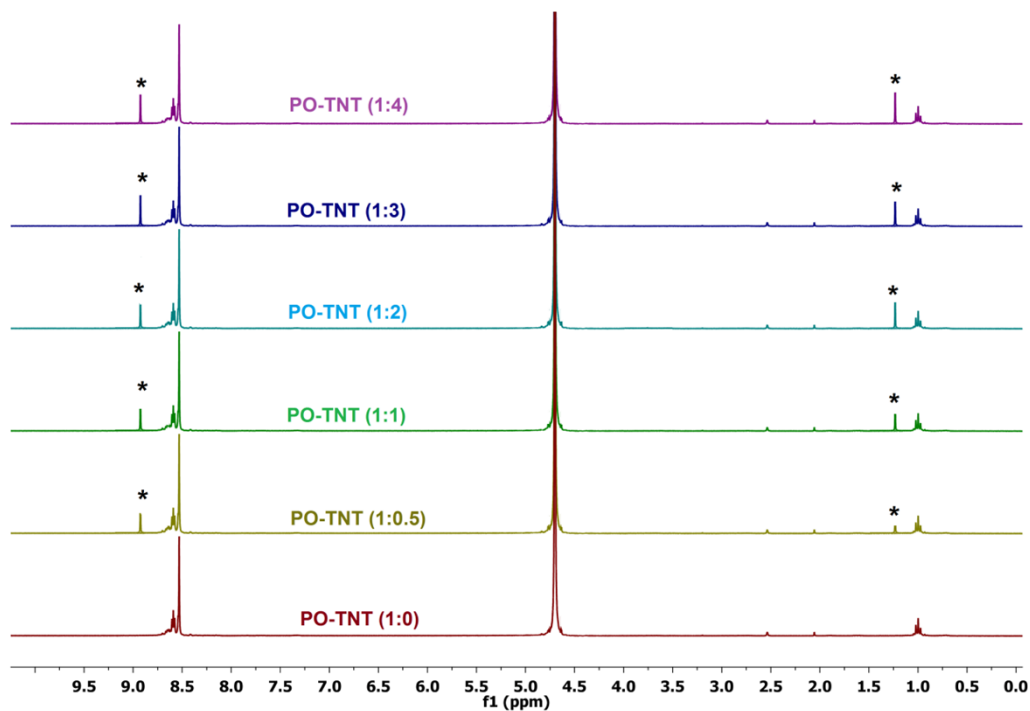


Fig. S30 ^1H NMR (300 MHz, D_2O) spectra of **PO** upon the addition of different mole ratios of TNT. The asterisks (*) represent the singlet peak belongs to TNT and appearing in the aromatic region, and $-\text{CH}_3$ protons in the high magnetic field region.

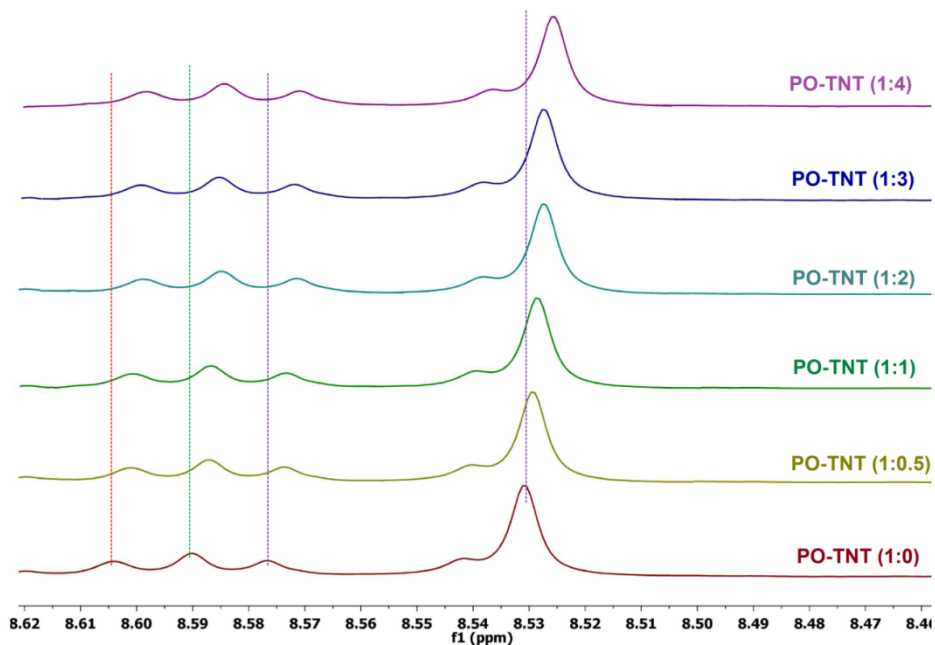


Fig. S31 Magnification of the ^1H NMR spectra of **PO** upon the addition of different mole ratios of TNT (in D_2O).

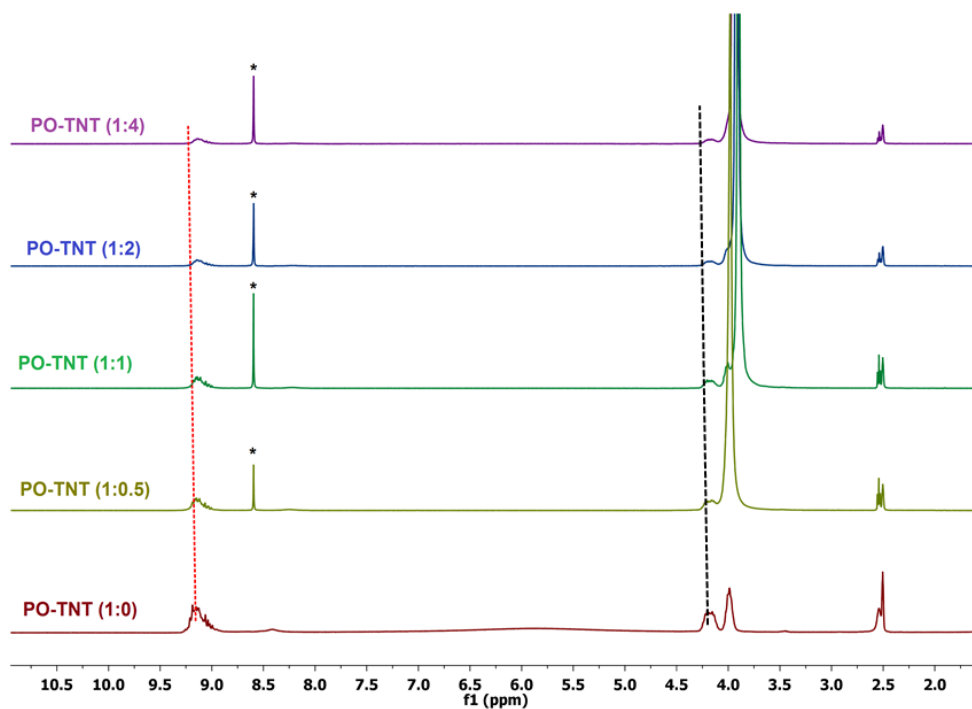


Fig. S32 ^1H NMR spectra of **PO** upon the addition of different mole ratios of TNT (in $\text{DMSO-}d_6$). The asterisk (*) represents the singlet peak belonging to TNT and appearing in the aromatic region.

13 Possible modes of interaction between PO and TNT

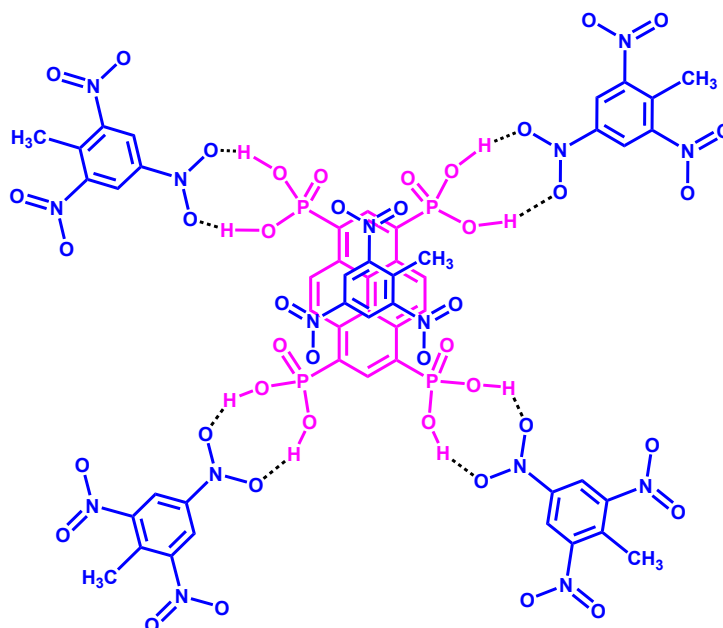


Fig. S33 Possible modes of interaction between **PO** and TNT.

14 Steady-state fluorescence emission spectra of thin films with NACs

Fluorescence experiments were performed at ambient temperature. Approximately 25 mg of NAC was placed inside a 10 mL vials and then a piece of cotton was placed onto top to prevent direct contact of films with NACs. Vials were kept closed for, at least, 5 days prior to carry out sensing experiments in order to assure that each NACs vapor reached equilibrium. The vapor pressure of NACs was varied according to the number and nature of nitro groups on benzene ring.⁶ Before exposing the spin-coated films to NACs vapors, emission of the film was recorded with a fluorescence spectrophotometer. The film was then placed onto the cotton piece in the vial and kept closed for a specific time. The film was then taken out of the vial and its emission recorded again. The saturated vapor pressure of TNT was *ca.* 10 ppb.⁶

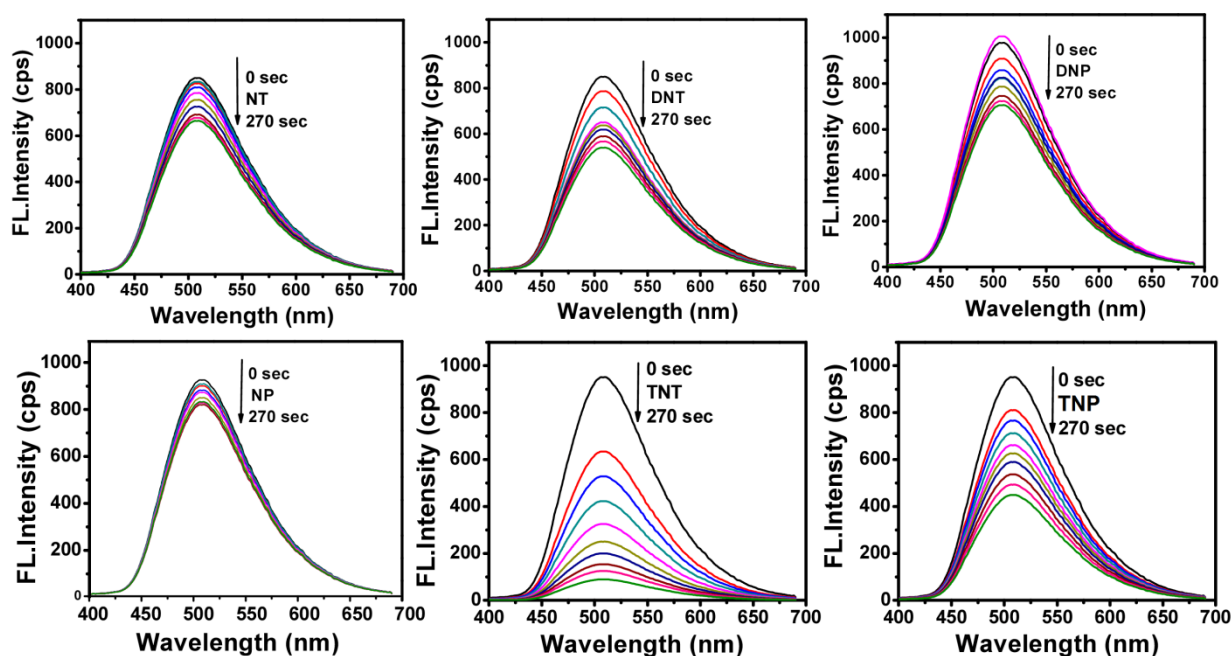


Fig. S34 Emission spectra of PE thin films exposed to saturated vapors of various NACs at different time intervals with $\lambda_{\text{ex}} = 370$ nm.

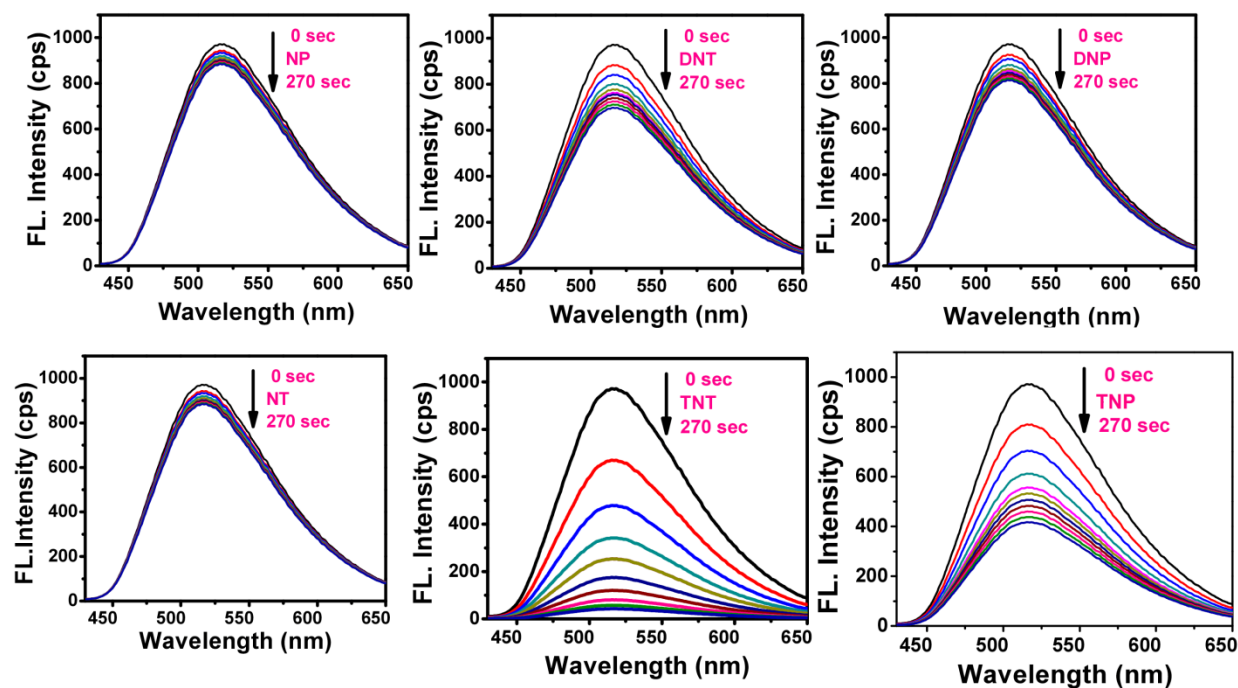


Fig. S35 Emission spectra of **PO** thin films exposed to saturated vapors of various NACs at different time intervals with $\lambda_{\text{ex}} = 370$ nm.

15 Reversibility

Reversibility tests of the **PE** and **PO** film towards the detection of TNT were carried out. Films were exposed to saturated vapors of TNT at ambient temperature for 180 s for **PE** and 90s for **PO** and the emission spectrum was recorded. The film was then washed (with methanol for **PE** and chloroform for **PO**) and dried at 45 °C under vacuum; the emission spectrum was once again recorded and the whole process repeated. Results indicate that the initial fluorescence intensity was maintained after several washings, thereby indicating high photo-stability of the prepared films.

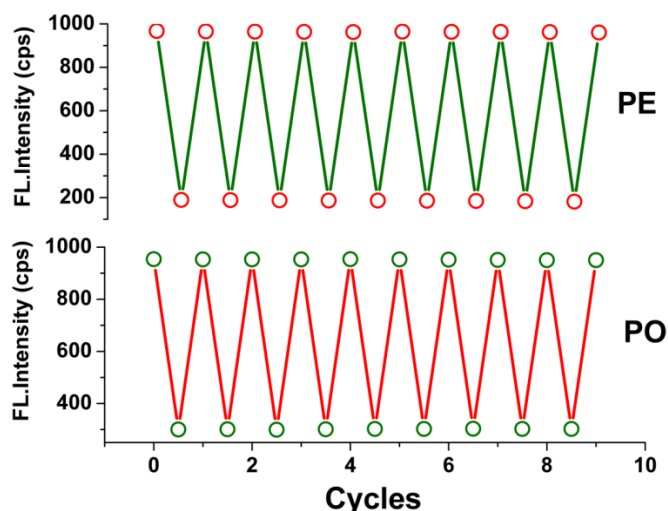


Fig. S36 Reversibility tests of **PE** and **PO** thin films to the saturated vapors of TNT for 180 sec (**PE**) and 90 sec (**PO**) of exposure time.

16 Visual detection

The visual detection of detection was carried out by coating the both PE and PO on whatman filter paper as test strips. 1×10^{-5} M solution of PE and PO was prepared and the test strips of dimension $3 \times 3 \text{ cm}^2$ was taken and immersed into the solution to absorb the solution uniformly. After 2 min, the test strips were taken out and dried. The test strips were now placed into the stock solution of known concentration of NACs. The image of the test strip was collected under UV light illumination at 365 nm before and after immersion into stock solution of NACs. The representative visual change in the turn off fluorescence behaviour of test strips treated with 2 ppb of TNT solution.

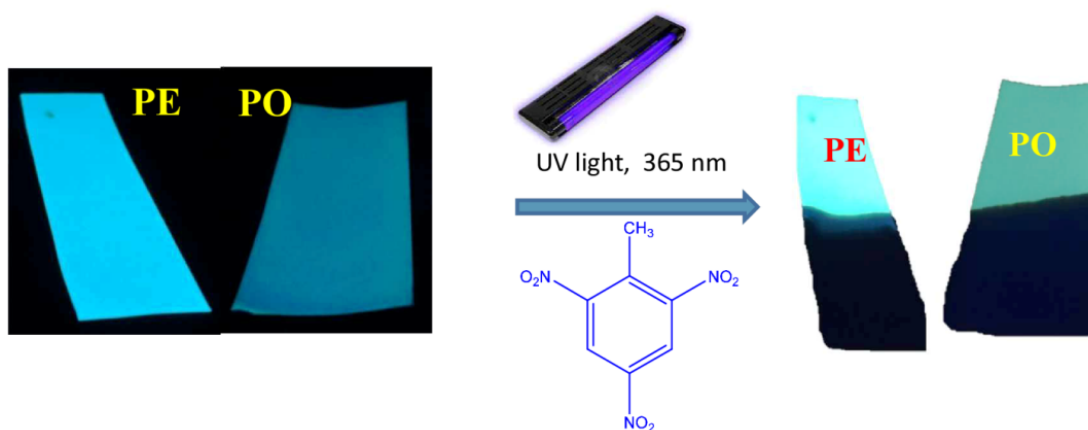


Fig. S37 Photographs of test paper strips that were first impregnated with compounds PE and PO (1×10^{-5} M) then dipped into a TNT solution (2 ppb), viewed under 365 nm UV light.

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